OXYGEN REDUCTION AT POLYPYRROLE ELECTRODES—I. THEORY AND EVALUATION OF THE RRDE EXPERIMENTS

R. C. M. JAKOBS, L. J. J. JANSSEN and E. BARENDRECHT

Laboratory for Electrochemistry, Department of Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 20 November 1984; in revised form 19 January 1985)

Abstract—The rotating ring-disc electrode (rrde) is used to determine the heterogeneous reaction rate constants for the cathodic reduction of molecular oxygen at a polypyrrole electrode in 0.5 M H₂SO₄. During the rrde experiments, a substantial concentration of hydrogen peroxide is built up in the bulk electrolyte. The theory is adapted to these circumstances and from the results, the various reaction rate constants are calculated. In the modified theory, the bulk peroxide is used to determine the activity of the ring electrode and it is possible to correct the ring current in situations where no diffusion limitation of the peroxide oxidation occurs.

NOMENCLATURE

\( A_d \) disc surface area m²
\( A_r \) ring surface area m²
\( b \) slope of \( 1/I_r \) vs \( 1/\sqrt{J} \) A⁻¹ s⁻¹/²
\( c \) concentration M, mol m⁻³
\( D \) diffusion coefficient m² s⁻¹
\( E \) potential V
\( E_d \) disc potential V
\( E_r \) ring potential V
\( F \) Faraday's constant C mol⁻¹
\( f \) (rotation) frequency Hz
\( I_{D}(H_2O) \) disc current leading to water A
\( I_{D}(H_2O_2) \) disc current leading to hydrogen peroxide A
\( I_{D,l} \) limiting disc current A
\( I_r \) ring current A
\( I_{R,0} \) ring current at \( E_D = 0.80 \) V, A
\( I_{R,l} \) limiting ring current A
\( I_{R,l} \) limiting ring current at \( E_D = 0.80 \) V, A
\( k \) heterogeneous reaction rate constant m s⁻¹
\( \delta \) thickness of the polymer film m
\( \eta \) collection efficiency
\( \sigma \) number of electrons involved in overall electrode reaction equation
\( p(H_2O) \) water formation efficiency
\( Q \) charge passed during film formation per unit geometrical surface area C m⁻²
\( T \) absolute temperature K
\( \nu \) kinematic viscosity m² s⁻¹

Superscripts

\( ad \) adsorbed
\( f \) polymer film
\( s \) bulk
\( \sigma \) interphase metal/polypyrrole

1. INTRODUCTION

The reduction of molecular oxygen is not only an important reaction in biological systems, but is also intensively studied for improving energy conversion systems such as electrochemical fuel cells. In an electrochemical fuel cell, the oxygen molecule is reduced electrochemically, i.e., by cathodic reduction[1] and the electrocatalysis at the oxygen electrode is of great importance.

In order to investigate the electrocatalytical aspects of the cathodic oxygen reduction at polypyrrole-covered electrodes (denoted PP electrodes), measurements have been carried out, using a rotating ring-disc electrode (rrde).

For some reaction mechanisms, like that of the oxygen reduction, the mathematics of the rrde has been extensively developed[2-4], which makes the determination of heterogeneous reaction rate constants possible when the bulk of the electrolyte contains virtually no hydrogen peroxide. However, for the reaction mechanism proposed in this study and in the case of the presence of a substantial amount of hydrogen peroxide in the bulk of the electrolyte, the mathematics of the rrde has not yet been elaborated and is given below.

2. THEORY

It is found[5] that the following steps for the reduction of oxygen at a polypyrrole (PP) electrode occur in sequence: diffusion of dissolved oxygen to and through the polymer layer, cathodic reduction of molecular oxygen, probably at the metal/polypyrrole interface, giving H₂O and/or H₂O₂.

The hydrogen peroxide formed either diffuses back to the bulk of the electrolyte through the PP layer or decomposes to H₂O and O²⁻. The latter is immediately reduced to water via

\[ \text{O}_2^- + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}. \]

The total reaction scheme is given in Fig. 1, in which \( s \) denotes the bulk of the electrolyte and \( \sigma \) the interphase metal/polypyrrole. \( D^s \) and \( D^f \) denote the diffusion coefficients in respectively the bulk electrolyte and the polymer film, while the subscripts for \( D \) and \( c \) refer to the molecular oxygen (1) and hydrogen peroxide (2).
During the oxygen reduction measurements, a peroxide concentration is built up in the bulk electrolyte. This means that the theory developed by Pleskov and Filinovskii in order to determine the rate constants \( k_1, k_2 \) and \( k_3 \), is not applicable, since it demands a virtually peroxide-free bulk electrolyte.

When the bulk peroxide is taken into account, the mass balances at the polypyrrole-covered disc are:

For \( \text{O}_2 \):

\[
D_1 \frac{c_i^1 - c_i^s}{\delta'_1} = c_i^1 (k_1 + k_3)
\]  

(1)

The second right-hand term in Equation (7) represents the ring current resulting from bulk peroxide. To simplify Equation (7), this term is substituted by \( I_{R,L}^0 \), which only depends on \( f \) in a given electrolyte at a given temperature.

So, Equation (7) becomes

\[
I_{R,L}^0 = 2NA_FD \frac{c_i^s - c_i^*}{\delta_2}
\]  

(8)

From Equations (1), (2) and (6) it follows for \( I_D \)

\[
I_D = 2A_F \frac{2k_1 k_2 c_i^1}{k_1 + k_3} \frac{k_1 + k_2 + k_3}{k_1 + k_2 + k_3}
\]

(9)

and from Equations (1), (2) and (7)

\[
I_{R,L}^0 = 2NA_F \frac{2k_1 k_2 c_i^1}{k_1 + k_3} \frac{k_1 + k_2 + k_3}{k_1 + k_2 + k_3}
\]

(10)

Equations (3), (4), (9) and (10) give

\[
\frac{1}{I_D + \left( \frac{I_{R,L}^0}{N} \right)} = \frac{1}{4A_F c_i^1} \left[ \frac{1}{k_1 + k_3} + \frac{l}{D_i^1} + \frac{\gamma_i}{4A_F D_i^1 c_i^1 \sqrt{2\pi \sqrt{f}}} \right]
\]

(11)

and for \( \text{H}_2\text{O}_2 \):

\[
c_i^1 k_2 + D_i^2 \frac{c_i^1 - c_i^s}{\delta_2} = c_i^s k_3
\]

(2)

with [7, 8]

\[
\delta'_i = \delta_i \frac{D_i^1}{D_i^2}
\]

(3)

\[
\delta_i = \frac{\gamma_i}{\sqrt{2\pi \sqrt{f}}}
\]

(4)

and

\[
\gamma_i = 1.61 (D_i^1)^{1/3} \nu^{1/6}.
\]

(5)

In the above equations, \( D \) is the diffusion coefficient \((m^2 s^{-1})\), \( c \) is the concentration \((mol m^{-3})\), \( l \) is the polypyrrole layer thickness \((m)\), \( \delta \) is the rrde diffusion layer thickness for component \( i \) \((m)\), \( \nu \) is the kinematic viscosity of the solution \((m^2 s^{-1})\) and \( f \) is the rotation frequency of the electrode \((Hz)\).

When the ring is kept at a potential where \( \text{H}_2\text{O}_2 \) is oxidized under conditions of diffusion limitation, the disc and ring currents are, respectively

\[
I_D = -A_F \left[ (4k_1 + 2k_2) c_i^1 + 2k_3 c_i^s \right]
\]

(6)

and

\[
I_{R,L} = 2NA_F F \frac{c_i^s - c_i^*}{\delta_2} + 2A_F \frac{c_i^s}{\delta_2}
\]

(7)

where \( I_D \) is the disc current \((A)\), \( A_F \) is the disc surface area \((m^2)\), \( F \) is the Faraday \((C mol^{-1})\), \( I_{R,L} \) is the diffusion limited ring current \((A)\), \( N \) is the rrde collection efficiency[9], \( A_R \) is the ring surface area \((m^2)\) and \( \delta_{2,R} \) is the diffusion layer thickness for peroxide at the ring electrode \((m)\).

The second right-hand term in Equation (7) represents the ring current resulting from bulk peroxide. To simplify Equation (7), this term is substituted by \( I_{R,L}^0 \), which only depends on \( f \) in a given electrolyte at a given temperature.

So, Equation (7) becomes

\[
I_{R,L}^0 = 2NA_F D_i^1 \frac{c_i^s - c_i^*}{\delta_2}
\]

(8)

Equation (11) shows that, when \( y = 1/(I_D + (I_{R,L}^0 - I_{R,L}^0)/N) \) is plotted against \( 1/\sqrt{f} \), a straight line is obtained with slope

\[
S_1 = \frac{1}{4A_F c_i^1} \left[ \frac{1}{k_1 + k_3} + \frac{l}{D_i^1} + \frac{\gamma_i}{4A_F D_i^1 c_i^1 \sqrt{2\pi \sqrt{f}}} \right]
\]

(12)

and intercept with the \( y \)-axis at \( 1/\sqrt{f} = 0 \)

\[
Y_1 = \frac{1}{4A_F c_i^1} \left[ \frac{1}{k_1 + k_2 + l}{D_i^1} \right]
\]

(13)

Rearrangement of Equation (13) gives

\[
(k_1 + k_2) = \frac{1}{4A_F c_i^1 Y_1} \frac{l}{D_i^1}
\]

(14)
Equations (3), (9) and (10) give

$$\frac{-I_D}{I_{R,i} - I_{R,i}^{0}} = \frac{1}{N} \left( \frac{2(k_1 + k_2)(k_3 \frac{l}{D_1} + 1) c_1^2 + 2(k_1 + k_2) k_3 c_1^2 \frac{\delta_2}{D_2}}{k_2 c_1^2 - k_3 c_2^2 - (k_1 + k_2) k_3 c_2^2 \frac{l}{D_1} - (k_1 + k_2) k_3 c_2^2 \frac{\delta_2}{D_2}} - 1 \right)$$  \quad (15)

or, in another way, using Equation (4)

$$\frac{-I_D}{I_{R,i} - I_{R,i}^{0}} = \frac{1}{N} \left( \frac{a_1 + b_1}{a_2 + b_2} \frac{1}{\sqrt{f}} - 1 \right)$$  \quad (16)

with

$$a_1 = 2(k_1 + k_2) \left( k_3 \frac{l}{D_1} + 1 \right) c_1^2,$$

$$b_1 = 2(k_1 + k_2) k_3 c_1^2 \frac{\gamma_2}{D_2} \sqrt{2\pi},$$

$$a_2 = k_2 c_1^2 - k_3 c_2^2 - (k_1 + k_2) k_3 c_2^2 \frac{l}{D_1},$$

$$b_2 = -(k_1 + k_2) k_3 c_2^2 \frac{\gamma_1}{D_1} \sqrt{2\pi}.$$

When the condition

$$\left| \frac{1}{\sqrt{f}} \right| \approx |a_2|$$  \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ Quad
defined above, \( I_D(H_2O) \) and \( I_D(H_2O_2) \) are given by

\[
I_D(H_2O) = -4p(H_2O)A_D Fm \tag{26}
\]
and

\[
I_D(H_2O_2) = -2[1 - p(H_2O)] A_D Fm. \tag{27}
\]

\( I_D(H_2O_2) \) is also given by

\[
I_D(H_2O_2) = - \frac{I_{R,i} - I_{R,i}^0}{N}. \tag{28}
\]

Combination of the Equations (25)-(28) gives for the water formation efficiency at a given rotation frequency

\[
N \frac{-I_D}{I_{R,i} - I_{R,i}^0} - 1 = \frac{p(H_2O)}{N} \frac{I_D}{I_{R,i} - I_{R,i}^0} + 1. \tag{29}
\]

The mean number of electrons, \( n_a \), for reduction of one oxygen molecule, defined by \( I_D = -n_a A_D Fm \) is found by combination of Equations (25)-(27)

\[
n_a = 2[p(H_2O) + 1]. \tag{30}
\]

When the oxygen reduction occurs under the condition of diffusion limitation in the electrolyte phase and with \( n_a \) electrons per \( O_2 \) molecule, the disc current is given by the Levich equation\([11]\]

\[
I_{D,i} = -0.62n_a A_D F(D_i^2)^{1/3} v^{-1/6} c_i^{1/2} \sqrt{2\pi f}. \tag{31}
\]

The ratio \( I_D/I_{D,i} \) gives an idea to which extend the condition of diffusion limitation in the electrolyte phase is reached. This ratio and \( p(H_2O) \) are used to characterize the polypyrrole electrode\([5]\).

### 3. Evaluation of the RRDE Data

As an example of the determination of \( k_1, k_2 \) and \( k_3 \), an outline of the evaluation of the RRDE data will be given. The data presented here are obtained from an oxygen reduction experiment, using a Pt disc/Pt ring RRDE in \( O_2 \)-saturated 0.5 M H_2SO_4 at a temperature of 293 K. The disc was covered with a polypyrrole layer which was formed by electropolymerization as described in\([10]\). The polymer film was formed at 298 K, 100 kPa and at a constant formation potential of 1.20 V vs see. The formation charge of the polypyrrole film was 0.60 kC m^{-2}, which gives a layer thickness of \( l = 1.7 \times 10^{-7} \) m when Equation (10) in\([10]\) is used. During the RRDE experiments, the disc potential was determined by triangular potential sweep with a potential scan speed \( v_D = 0.05 \) V s^{-1}, while the ring was kept at a constant peroxide detection potential, namely \( E_R = 1.25 \) V. The rotation frequency \( f \) of the RRDE was varied from 0 up to 81 Hz. The ring and disc currents were plotted against the disc potential using a dual-pen X-Y-recorder. The potentials were measured with respect to the reversible hydrogen electrode in 0.5 M H_2SO_4.

Figure 2 shows the ring and disc current curves for the potential sweep experiment at \( f = 81 \) Hz. From the \( I_D - E_D \) curve in Fig. 2 it follows that diffusion limitation of the reduction current occurs for \( E_D < 0.15 \) V.

The ring current curve shows an increasing peroxide detection current with decreasing disc potential for \( E_D < 0.70 \) V. For \( E_D > 0.70 \) V, the ring current is nearly independent of the disc potential, which indicates that no peroxide is formed at the disc. The practically constant ring current for \( E_D > 0.70 \) V is caused by the

![Fig. 2. O_2 reduction at a Pt disc/Pt ring RRDE in O_2-saturated 0.5 M H_2SO_4. Disc covered with polypyrrole (\( Q = 0.6 \) kC m^{-2}) and aged for 48 h at \( E_D = 0.2 \) V, \( v_D = 0.05 \) V s^{-1}, \( E_R = 1.25 \) V, \( f = 81 \) Hz, \( T = 293 \) K.](image_url)
oxidation of peroxide present in the bulk of the solution.

Table 1 shows the disc and ring currents in O2-saturated 0.5 M H2SO4 at E = 0.10 V and E = 0.30 V at various rotation frequencies f. The currents are obtained from sweep curves like that in Fig. 2, recorded at various rotation frequencies. The ring and disc currents originate from the curves for increasing disc potential (ie the anodic scan).

At E = 0.80 V, ie the potential at which absence of peroxide production or consumption at the disc is assumed, I$D$ is obtained for each rotation frequency. Table 2 gives the data which are additionally needed for the calculation of the rate constants. The oxygen saturation concentration c$_{O2}$ in 0.33 M H2SO4 was found in the literature[14].

In 0.5 M H2SO4, c$_{O2}$ at 293 K is 1.03 mol m$^{-3}$[13]. By multiplication of the oxygen concentrations in 0.33 M H2SO4 and at various temperatures with a factor 1.03/1.30 = 0.792, the corresponding concentrations in 0.5 M H2SO4 were calculated.

The oxygen diffusion coefficient D$_O$ in 0.5 M H2SO4 was determined as a function of the temperature by means of polarography.

The result for D$_O$ at 293 K was in agreement with the value of 2.1 x 10$^{-9}$ m$^2$s$^{-1}$, found in the literature[14].

After rotating-disc measurements with diffusion limited reduction of oxygen and hydrogen peroxide, it appeared that, at 293 K, D$_O$/D$_O$ = 0.70. Assuming that this ratio is constant over the whole temperature range, D$_O$ can be calculated from D$_O$ at each temperature.

The kinematic viscosity $\nu$ was calculated using literature data[15, 16]. First, 1/I$D_D$ is plotted against 1/$\sqrt{f}$, see Fig. 3. This plot gives a straight line with a slope b = 7.06 x 10$^{-9}$ A$m^{-1}$s$^{-1/2}$ and a positive intercept with the 1/I$D_D$-axis at 1/$\sqrt{f}$ = 0. The intercept indicates that the peroxide detection current at the ring electrode is not pure diffusion limited, since in that case, the straight line in Fig. 3 would pass through the origin.

The fact that the plot in Fig. 3 gives a straight line indicates that the catalytical decomposition of peroxide at the disc can be neglected. This conclusion is confirmed by separate measurements using a PP-covered Pt disc in deoxygenated, peroxide-containing 0.5 M H2SO4[5].

Since the ring electrode is calibrated in a separate experiment, using 0.5 M H2SO4, containing various amounts of hydrogen peroxide (determined by permanganometry), the bulk concentration of peroxide can be calculated from the slope b of the 1/I$D_D$ vs 1/$\sqrt{f}$ curve.

From the slope b in Fig. 3 it follows that c$_2$ = 0.174 mol m$^{-3}$.

The diffusion limited ring current at E = 0.80 V, I$D_R$ can be calculated at each frequency from Fig. 3 using

\[ I_{D,R} = \frac{\sqrt{f}}{b}. \]  \hspace{1cm} (32)

In Fig. 3, Equation (32) represents a straight line passing through the origin and with a slope b. In an alternative way, I$D_R$ can be calculated from I$D_R$ by multiplication of I$D_R$ with a "correction factor" for each rotation frequency, given by

\[ \text{correction factor} = \frac{\sqrt{f}}{bI_{D,R}}. \]  \hspace{1cm} (33)

It is likely that the correction factor in Equation (33) is independent of the peroxide concentration, so it can be used to calculate the diffusion limited ring current, I$D_{R,lim}$, from the ring currents that are not diffusion limited. This procedure is also useful for other potentials than E = 0.80 V. So, the diffusion limited ring current I$D_{R,lim}$ at a given rotation frequency is obtained from

\[ I_{D,R,lim} = I_{D,R} \frac{\sqrt{f}}{bI_{D,R}}. \]  \hspace{1cm} (34)

The values for I$D_R$ and I$D_{R,lim}$, obtained at each rotation frequency in the way mentioned above, are used to plot 1/[E - I$D_R$ + (I$D_{R,lim}$ - I$D_{R,lim}$)/N] vs 1/$\sqrt{f}$, the result of which is given in Fig. 4 for E = 0.10 V. The plot has a

<table>
<thead>
<tr>
<th>T</th>
<th>c$_{O2}$</th>
<th>D$_O$</th>
<th>D$_O$</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>mol m$^{-3}$</td>
<td>(10$^{-9}$ m$^2$s$^{-1}$)</td>
<td>(10$^{-9}$ m$^2$s$^{-1}$)</td>
<td>(10$^{-6}$ m$^2$s$^{-1}$)</td>
</tr>
<tr>
<td>293</td>
<td>1.03</td>
<td>2.1</td>
<td>1.5</td>
<td>1.07</td>
</tr>
<tr>
<td>308</td>
<td>0.76</td>
<td>3.7</td>
<td>2.6</td>
<td>0.77</td>
</tr>
<tr>
<td>323</td>
<td>0.58</td>
<td>6.3</td>
<td>4.4</td>
<td>0.58</td>
</tr>
<tr>
<td>338</td>
<td>0.46</td>
<td>9.0</td>
<td>7.1</td>
<td>0.48</td>
</tr>
</tbody>
</table>

$A_D = 5.046 \times 10^{-2}$ m$^2$

$F = 9.65 \times 10^4$ C mol$^{-1}$

$N = 0.241$

\[ I = 1.7 \times 10^{-7} \text{ m} \]
Fig. 3. Plot of $1/I_R^0 vs 1/\sqrt{f}$ for O$_2$ reduction at a PP(Pt)/Pt rde in O$_2$-saturated 0.5 M H$_2$SO$_4$. $E_R = 0.80$ V, $E_D = 1.25$ V, $T = 293$ K. Slope: $b = 7.06 \times 10^4$ A$^{-1}$ s$^{-1/2}$. Intercept at $1/\sqrt{f} = 0$: $Y_1 = 6.50 \times 10^3$ A$^{-1}$.

slope: $S_1 = 1.71 \times 10^3$ A$^{-1}$ s$^{-1/2}$ and an intercept at $1/\sqrt{f} = 0$: $Y_1 = 3.95 \times 10^2$ A$^{-1}$.

From the slope $S_1$ and Equation (12), the oxygen concentration in the bulk of the electrolyte is calculated, resulting in $c_1' = 1.19$ mol m$^{-3}$, which reasonably corresponds to the concentration of 1.03 mol m$^{-3}$ in Table 2. At $E_D = 0.10$ V, the disc current is limited by diffusion of oxygen originating from the bulk of the solution (Fig. 2). This means that, at $E_D = 0.10$ V, $1/(k_1 + k_2) \ll I/D_1'$ and using Equation (23) with $c_1' = 1.03$ mol m$^{-3}$, it follows that $I/D_1' = 7.92 \times 10^{-5}$ m$^{-2}$ s$^{-1}$. With $l = 1.7 \times 10^{-3}$ m, this gives $D_1' = 2.1 \times 10^{-11}$ m$^2$ s$^{-1}$ and, using Equation (20), $D_1' = 1.5 \times 10^{-11}$ m$^2$ s$^{-1}$.

Subsequently, $1/[I - I_D + (I_{R1} - I_{R0}^0)/N]$ is plotted against $1/\sqrt{f}$ for the other disc potentials. Figure 5 gives this plot for $E_D = 0.30$ V. The plot has a slope: $S_1 = 1.87 \times 10^3$ A$^{-1}$ s$^{-1/2}$ and an intercept at $1/\sqrt{f} = 0$: $Y_1 = 6.20 \times 10^2$ A$^{-1}$.

The slope $S_1$ gives with Equation (12) a bulk oxygen concentration $c_1' = 1.09$ mol m$^{-3}$. The intercept $Y_1$ and Equation (14) give for $E_D = 0.30$ V: $k_1 + k_2 = 2.21 \times 10^{-4}$ m$^{-1}$ s$^{-1}$.

Figure 6 presents the plot of $-I_D/(I_{R1} - I_{R0})$ against $1/\sqrt{f}$ for the data at $E_D = 0.30$ V. The plot is a straight line with slope $S_2 = 3.62$ s$^{-1/2}$ and intercept at $1/\sqrt{f} = 0$: $Y_2 = 5.90$. The fact that the plot in Fig. 6 fits well to a linear relationship between $-I_D/(I_{R1} - I_{R0})$ and $1/\sqrt{f}$, means that condition (17) will be satisfied and Equations (18) and (19) may be used.

Together with the results found for $(k_1 + k_2)$, $I/D_1'$ and $c_1'$, Equation (17) gives $k_3 = 7.9 \times 10^{-6}$ m s$^{-1}$. Equation (19) gives $k_2 = 2.0 \times 10^{-4}$ m s$^{-1}$, so $k_1 = 2.1 \times 10^{-5}$ m s$^{-1}$.

After $k_1$, $k_2$ and $k_3$ have been calculated, it is necessary to check whether or not the condition (17) is satisfied. It appears for the experiment at $E_D = 0.30$ V, used in this outline, that in Equation (16), $b_2 = 1.2 \times 10^{-5}$ mol m$^{-2}$ s$^{-3/2}$ and $a_2 = 2.0 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$. So, condition (17) is satisfied for the rotation frequency range used in the experiment described here, viz $1$ Hz < $f$ < 81 Hz.

Fig. 4. Plot of $1/[I - I_D + (I_{R1} - I_{R0}^0)/N]$ vs $1/\sqrt{f}$ for O$_2$ reduction at a PP(Pt)/Pt rde in O$_2$-saturated 0.5 M H$_2$SO$_4$. $E_R = 0.80$ V, $E_D = 1.25$ V, $T = 293$ K. Slope: $S_1 = 1.71 \times 10^3$ A$^{-1}$ s$^{-1/2}$. Intercept at $1/\sqrt{f} = 0$: $Y_1 = 3.95 \times 10^2$ A$^{-1}$.

Fig. 5. Plot of $1/[I - I_D + (I_{R1} - I_{R0}^0)/N]$ vs $1/\sqrt{f}$ for O$_2$ reduction at a PP(Pt)/Pt rde in O$_2$-saturated 0.5 M H$_2$SO$_4$. $E_D = 0.30$ V, $E_R = 1.25$ V, $T = 293$ K. Slope: $S_1 = 1.87 \times 10^3$ A$^{-1}$ s$^{-1/2}$. Intercept at $1/\sqrt{f} = 0$: $Y_1 = 6.20 \times 10^2$ A$^{-1}$. 
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4. DISCUSSION

It is shown that the calculation of the heterogeneous reaction rate constants for the cathodic oxygen reduction in hydrogen peroxide-containing electrolyte is possible using the rrde measuring technique. When condition (17) is satisfied, the calculation of \( k_1, k_2 \) and \( k_3 \) is straightforward. Whether or not condition (17) is satisfied mainly depends on the bulk concentration of hydrogen peroxide, \( c_2 \), and the kinetics of the oxygen electrode, \( v \), viz \( k_1, k_2 \) and \( k_3 \).

For the remaining situations, a numerical approach of Equation (15) will lead to the determination of the rate constants.

The hydrogen peroxide, present in the bulk of the electrolyte, makes it possible to correct the ring currents in cases where these currents are not purely limited by diffusion of hydrogen peroxide towards the ring electrode. This means that the ring electrode can be used without preceding platination, which avoids the problem of decreasing ring activity during rrde measurements due to poisoning of the platinum black on the ring.

REFERENCES

7. Ref. [4], p. 305.